

Thermal testing methods in determination of characterization of charcoals

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ABSTRACT Thermal analysis testing methods were used in determination of the characterization of charcoals. Thermogravimetry (TG) method was adopted to determine the composition of charcoals, which include moisture, volatiles, fixed carbon and ash contents. The result showed that this method could detect the subtle change of charcoal composition, even the variation of different parts of material. Differential Thermal Analysis (DTA) and related methods were also used to investigate reactivity of charcoals. The ignition temperature decrease with increasing carbon content was detected by these methods.

Key words: Thermal analysis, Charcoal, Ignition temperature, Thermogravimetry, Differential thermal analysis

Introduction

Charcoal, produced by the partial pyrolysis of wood in an inert atmosphere, is a complex material of which the physical and chemical characteristics may vary widely. The properties may vary with the type of wood used, the part of the tree from which the wood is cut, as well as the pyrolysis regime to which the wood is subjected. The aim of the present work is to develop a range of tests for the characterization of composition and reactivity of charcoals for use in gunpowder.

Compositional analysis by thermogravimetry (TG)

TG method is applicable to powdered samples or solid pieces of charcoal.

The moisture content is determined by heating a 5-mg sample to 110°C under nitrogen flowing at 25 cm³ min⁻¹, and holding isothermally for 5 minutes. The weight record is then expanded to 100% so that the other parameters can be read directly from the chart as percentages of the dry weight. The volatile content is determined by heating the sample to 750°C at a increasing rate of 20°C min⁻¹ and holding at this temperature for 3 minutes, during which stage, the weight

of sample losses due to the evolution of adsorbed volatile matter and further pyrolysis of oxyhydrocarbon functional groups attached to the biopolymer skeleton. A true weight plateau rarely develops at this stage, due partly to the protracted nature of the decomposition, and partly to oxidation of the highly reactive carbon remaining by the trace impurities in the purge gas. Although this could be overcome by using purified purge gas and longer isothermal time, the purpose of the test was to provide a rapid assessment of the composition, therefore the volatile content is empirically defined as the weight loss after the 3 minutes hold. After cooling to 200°C the purge gas is switched to air, and the sample is heated to 900°C at a increasing rate of 50 °C min⁻¹, then the carbon burns off leaving a weight corresponding to the ash content.

The compositional analysis was made by thermogravimetry (TG) in this study. A schematic diagram of a TG curve generated by this procedure is shown in Fig.1. The sharply increased weight of sample after inputting air was resulted from the adsorption of oxygen prior to the initiation of burning. Table 1 gives an illustration of the reproducibility of the method and the range of charcoal types encountered.

As the TG method requires the sample that is in small size, it enables us to study the variation in composition through a single stick of charcoal. Dissection of an ovoid-section stick of about 5 cm in diameter yielded 10 cubes of charcoals that average about 5 mg. The values obtained for the volatiles, fixed carbon and moisture contents, plotted as a function of distance from the edge (Fig. 2), showed the marked

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variation that can be observed even with such a small stick. The lower volatile content at the center of the wood can be explained by the fact that the secondary stage of wood pyrolysis (the pyrolysis of released tars) is exothermic (Cordero *et al.* 1991). The temperature in the center of the wood, a material of low thermal conductivity, was considerably higher than at the edges, resulting in a greater degree of pyrolysis (Liu 1997).

Table 1. Compositional analysis of various alder charcoals

Charcoal sample	Dry weight, %			
	Moisture	Volatiles	Fixed carbon	Ash
1	4.0±0.1	76.4±0.2	22.1±0.3	1.5±0.3
2	3.3±0.1	56.2±0.1	42.6±0.5	1.3±0.4
3	4.2±0.1	37.6±0.4	60.4±0.6	20.0±0.3
4	4.6±0.0	26.9±0.1	69.1±0.1	4.1±0.1

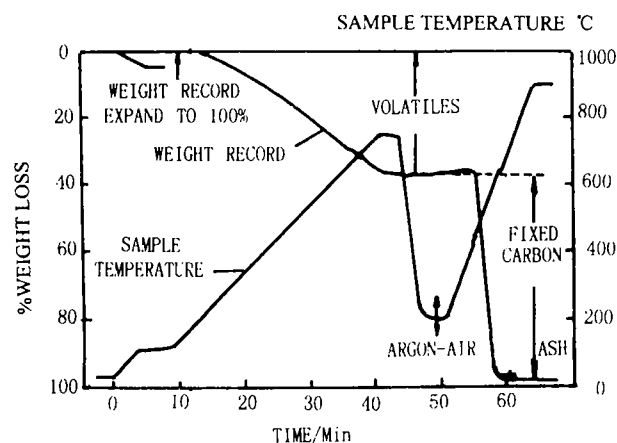


Fig. 1. Schematic diagram of the TG analysis curve for a charcoal

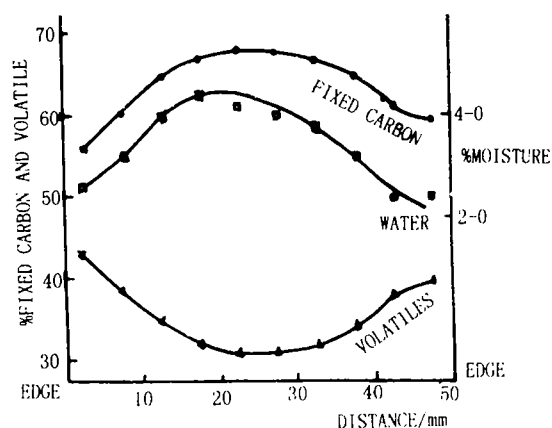


Fig. 2. Diametrical variation of properties through a charcoal stick

The trend with respect to moisture content was remarkably smooth. As all the samples had been stored

under similar conditions of temperature and humidity, this trend reflected the adsorptive capacity of the charcoal, and was clearly related to the degree of pyrolysis.

Differential thermal analysis (DTA)

Preliminary differential thermal analysis (DTA) method has been developed to determine the low temperature reactivity of charcoals (Zeriuoh *et al.* 1996; Kifani-Sahban Belkir *et al.* 1996). For defining the oxidation exotherm, the charcoals were dried under nitrogen flow in the instrument (Stanton Redcroft DTA-6718). The atmosphere was changed to flowing air before cooling and reheating samples. The results showed that slight variation in the chosen conditions would result in minimal variation in the measured parameters. The conditions of TDA chosen finally were a sample weight of 5.0 ± 0.1 mg, heating rate of $10^\circ\text{C min}^{-1}$, air flow rate of $50\text{ cm}^3\text{ min}^{-1}$ and DTA sensitivity of $500\text{ }\mu\text{V}$. The sample pan was lightly tapped and drying conditions for the sample were standardized at 120°C for 5 min in flowing nitrogen. The DTA curve recorded is exothermic reaction that is due largely to oxidation of the released volatiles. A schematic representation of the curve is given in Fig. 3, which shows the measured parameters of temperature T_0 , T_5 , T_{10} , T_{50} , at which temperatures the deviations of voltage of 5, 10 and $50\text{ }\mu\text{V}$ from the baseline were detected respectively. The peak temperature (T_p) was also measured. Preliminary work showed that T_5 and T_{10} appear to be the most useful in characterizing the variation in susceptibility to oxidation at low temperature. Calculations showed that a correction for the temperatures based on the calibration constant of the DTA unit was unnecessary within the range of values obtained.

Study of the effects of oxidation during air-drying of a particular charcoal proved that DTA method in detecting subtle changes in the charcoals is very useful. Samples of the charcoal were heated in an oven at the different temperatures for varied time, and run under the standard conditions on the DTA-6718 instrument. The results are given in Table 2.

Table 2. The effect of oven temperature and drying time on DTA Characteristics of charcoal

Oven Temperatures / $^\circ\text{C}$	Drying time / H	DTA Characteristics / $^\circ\text{C}$	
		T_5	T_{10}
120	0	135 ± 1	150 ± 1
	1	146 ± 1	162 ± 0.5
	24	164	182
	168	204	215
80	24	138 ± 1	153.5 ± 0.5
	168	145 ± 0	162.5 ± 0.5

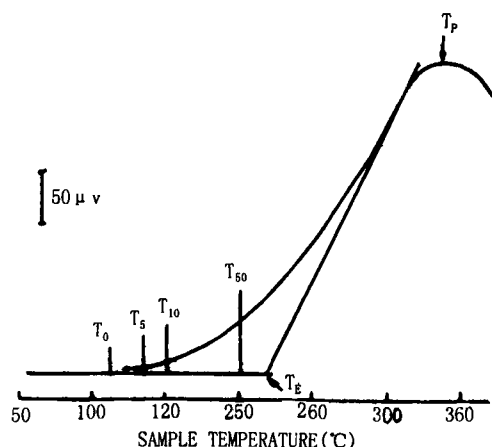


Fig. 3. Diagram of the DTA curve for oxidation of a charcoal

Other Tests

A number of other testing methods were also examined for application to charcoal testing. The reactivity of charcoal towards air at high temperatures was determined using a DTA head originally designed for determination of the ignition temperature of coals. The head consists of two fine gauze pans (15 mm in diameter), supported one above the other by mineral insulated chromel-alumel thermocouples. The head fits a standard DTA base (Stanton Redcroft DTA 673).

In order to determine the effect of carbon content on ignition temperature, 100 mg of sieved charcoal samples were heated at a temperature increasing rate of $20^{\circ}\text{C min}^{-1}$. At a flow rate of $500\text{ cm}^3\text{ min}^{-1}$, air passed over the sample which is contained in the upper pan. The ignition temperature of the charcoal is taken from the extrapolated onset of the deviation on the sample temperature trace, caused by combustion of the sample. The determined results of ignition temperature for Alder charcoals are given in Table 3.

Table 3. Effect of carbon content on Ignition Temperatures for Alder Charcoals

Carbon Content (%)	Ignition Temperature($^{\circ}\text{C}$)
61	245 ± 2
76	218 ± 1
82	212 ± 1
96	447 ± 1

The results show that the ignition temperature decreased with increasing of carbon content in range of 60~80%, but it showed a sharply increase when the percentage of carbon content was 96. This indicates that the ignition of sample starts at the time when the volatiles began to oxidize and stops at the time when the volatiles is insufficient to cause ignition.

DTG curves used to be used to distinguish similar

coals (Chen and Li 1985; Hirata *et al.* 1993; Ryoichi *et al.* 1993). With this method it is easy to distinct the charcoals with different carbon content, but it is difficult to differentiate between charcoals with similar carbon contents.

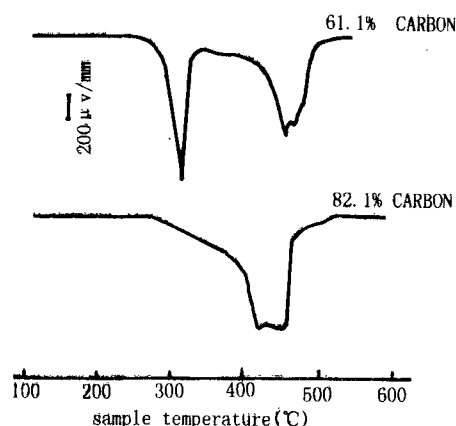


Fig. 4. DTG curve for Alder charcoal heated in air

TG-DTG-DTA methods were also simultaneously adopted to characterize the oxidative behavior of charcoal. The results indicated that oxidative behavior mainly depends on experimental parameters, particularly on compactness of sample, and it is also affected by carbon contents (see Fig. 4).

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